

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/18, 3/10	A1	(11) International Publication Number: WO 98/04662 (43) International Publication Date: 5 February 1998 (05.02.98)
(21) International Application Number: PCT/US97/12894 (22) International Filing Date: 23 July 1997 (23.07.97) (30) Priority Data: 9616076.7 31 July 1996 (31.07.96) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HALL, Robin, Gibson [GB/GB]; 27 Blackfriars Court, Stowell Street, Newcastle upon Tyne NE1 4XB (GB). VERMOTE, Christian, Leo, Marie [BE/GB]; 1 Kielder Way, Newcastle upon Tyne NE3 2LP (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A DETERGENT COMPOSITION COMPRISING AN ACID SOURCE WITH A SPECIFIC PARTICLE SIZE (57) Abstract A detergent composition comprising a detergent surfactant, a particulate acid source and an alkaline source wherein said acid source and alkaline source are capable of reacting together to produce a gas, and wherein about 80 % or more of the acid source has a particle size in the range of from about 150 microns to about 710 microns, with at least about 37 % by weight of the acid source having a particle size of about 350 microns or less.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TC	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

A DETERGENT COMPOSITION COMPRISING AN ACID SOURCE WITH A SPECIFIC PARTICLE SIZE**Technical Field**

5 The present invention relates to a detergent composition which is suitable for use in laundry and dish washing methods. The present invention also relates to a process for preparing these detergent powders.

Background to the Invention

10

There is a trend amongst commercially available granular detergents towards higher bulk densities and towards granular detergent compositions which have a higher content of detergent active ingredients. Such detergents offer greater convenience to the consumer and at the same time reduce the amount of packaging materials which will, ultimately, be disposed of.

15

Many of the prior art attempts to move in this direction have met with problems of poor solubility properties arising from low rate of dissolution or the formation of gels. A consequence of this in a typical washing process can be poor dispensing of the product, either from the dispensing drawer of a washing machine, or from a dosing device placed with the laundry inside the machine. This poor dispensing is often caused by gelling of particles, which have high levels of surfactant, upon contact with water. The gel prevents a proportion of the detergent powder from being solubilized in the wash water which reduces the effectiveness of the powder. This is a particular problem at low water pressures and/or at lower washing temperatures.

20

Further, there has been another recent trend towards reducing or eliminating the use of phosphate builders, which have generally been replaced with zeolite (crystalline aluminosilicate). Detergents containing zeolite builders have been found to be poorer dispensers than detergents containing phosphate builders.

25

EP-A-0 578 871 describes a process which seeks to make a high bulk density detergent composition which dissolves rapidly and dispenses effectively. The process involves formulating a base powder with a particle size distribution between 150 microns and 1700 microns in combination with additional filler ingredients whereby at least 20% by

30

weight of the filler particles is less than 150 microns. The filler particles include salts of citrate, sulphate, (bi-)carbonate and silicates.

5 WO95/14767 relates to the poor dispensing of high density, non-spray-dried detergent powders, and discloses the use of a citric acid salt which has a Rosin Rammler particle size of less than 800 microns.

10 WO94/28098 discloses a non-spray-dried detergent powder comprising a combination of an ethoxylated primary C8-18 alcohol, an alkali metal aluminosilicate builder and 5 to 40 wt% of a water-soluble salt of a citric acid.

15 EP-A-0 639 637 discloses the replacement of perborate bleach with an alkali metal percarbonate to improve the dispensing profile and dissolution rate of a detergent. Citrate or mixtures of citrate with sulphate or carbonate can be used to coat the percarbonate bleach.

EP-A-0 639 639 contains a similar disclosure in this respect.

20 Other ways to improve dispensing include the use of an effervescence system. If the detergent contains an effervescence system then the generation of a gas such as carbon dioxide pushes the particles of the detergent apart, and prevents them from gelling.

25 The use of effervescence to improve the dispersibility of granular materials has been used extensively in pharmaceutical preparations. The most widely used effervescent system in this respect is citric acid in combination with bicarbonate. The use of this simple effervescent system has also been described for improving the dispersibility of pesticidal compositions for controlling water-borne pests, e.g. GB-A-2,184,946.

30 US-A-4,414,130 discloses the use of a readily disintegratable builder particle with a zeolite-based detergent. It also discloses the use of an effervescence material to improve the dissolving and dissolution of the particles. Sodium carbonate or sodium bicarbonate may be combined with the zeolite binder mix and the balance of the detergent may include citric acid, monosodium phosphate, boric acid or other suitable acidifying material, preferably lated or agglomerated with bicarbonate, for reaction with it to generate carbon dioxide.

35

WO92/18596 discloses that improved solubility/dispersion for granular detergents can be achieved by admixing sodium carbonate and citric acid in a specified weight ratio of from 2:1 to 15:1.

- 5 EP-A-0 534 525 discloses the use of citric acid with a specified particle size range of 350 to 1500 microns.

US -A-5, 114,647 discloses a sanitising composition comprising granules of alkali metal carbonate and aliphatic carboxylic acid of a particle size of 150 to 2,000 microns.

10

EP-A-0 333 223 discloses a bathing preparation comprising fumaric acid having an average particle size of 50-500 microns.

- 15 We have now found surprisingly that improved dispensing benefits can be achieved from using citric acid which has a very specific particle size distribution and which is very different from that taught in the prior art. We have also found that surprisingly good storage stability is achieved with citric acid of with this same very specific particle size distribution; again this is very different from the teaching of the prior art.

- 20 The addition of citric acid results in a reduction in alkalinity. Such an alkaline pH promotes cleaning, stain removal and soil suspension, there is need to minimize the level of citric acid used. Also citric acid is a relatively expensive ingredient which further reinforces the need to keep the level of citric acid very low. We have also surprisingly found that the present invention allows low levels of the acid to be satisfactorily used in the detergent composition.
- 25

All documents cited in the present description are, in relevant part, incorporated herein by reference.

30

Summary of the Invention

- According to the present invention there is provided a detergent composition comprising a detergent surfactant, a particulate acid source and an alkaline source capable of reacting to produce a gas, wherein about 80% or more of the acid source has a particle size in the
- 35

range of from about 150 microns to about 710 microns, with at least about 37% by weight of the acid source having a particle size of about 350 microns or less.

5 We have found that the addition of the acid source in accordance with the particle size distribution of the present invention and an alkaline source to a detergent composition improves the solubility and/or dispersion of the detergent in the laundering solution and eliminates or reduces the problems of solid detergent particles remaining in the washing machine and on washed clothes. It is believed that the acid reacts rapidly with the alkali in the laundering solution to release the gas. This helps disperse the detergent and
10 minimize the formation of insoluble clumps.

Detailed Description of the Invention

15 The present invention includes a granular detergent composition. Such compositions comprise a base composition containing one or more surfactant, and preferably a builder material. The base composition may be prepared by spray-drying and dry-mixing/agglomeration. The base composition may also comprise the alkaline source. Alternatively the particulate acid source and/or alkaline source may be added as separate components to the detergent base composition, preferably in a granular form.

20 The detergent composition of the present invention comprises three essential ingredients: detergent surfactant, an acid source and an alkali source. These and optional ingredients, and processes for making the detergents, are described in detail below.

25 A. Detergent Surfactant

This ingredient is preferably present in an amount of from 1% to 90%, preferably 3% to 70%, more preferably 5% to 40%, even more preferably 10% to 30%, most preferably 12% to 25% by weight of the detergent composition. Preferably the detergent is selected
30 from anionics, nonionics, zwitterionics, ampholytics, amphoteric, cationics and mixtures thereof. Preferably the surfactant is anionic, nonionic or a mixture thereof. When the composition contains more than one surfactant the additional surfactant is preferably present at a level of from 0.1% to 50%, more preferably from 1% to 40%, most preferably from 5% to 30% by weight of the total surfactant present. Where present,
35 ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

- The surfactant system may include an anionic surfactant. Essentially any anionic surfactants useful for deterative purposes are suitable. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.
- Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

- Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

- Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

5 Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol
10 sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

15 Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula RO(CH₂CH₂O)_x
20 CH₂COO-M⁺ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula RO-(CHR₁-CHR₂-O)_x-R₃ wherein R is a
25 C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

30 Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may
35 also be included as suds suppressors.

Alkali metal sarcosinate surfactant

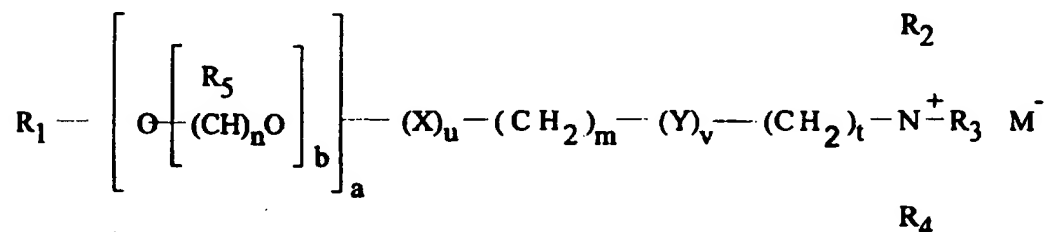
- Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R¹)CH₂COOM, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Cationic ester surfactant

- The surfactant system may include a cationic ester surfactant. That is, a preferably water dispersible compound having surfactant properties comprising at least one ester (ie -COO-) linkage and at least one cationically charged group.

- Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

Preferred cationic ester surfactants are those having the formula:

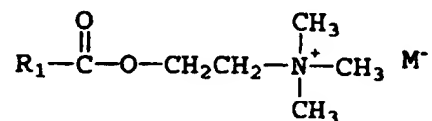


- wherein R₁ is a C₅-C₃₁ linear or branched alkyl, alkenyl or alkaryl chain or M⁺N⁺(R₆R₇R₈)(CH₂)₅; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R₂, R₃, R₄, R₆, R₇, and R₈ are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxy-alkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R₅ is independently H or a C₁-C₃ alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

Preferably R₂, R₃ and R₄ are independently selected from CH₃ and -CH₂CH₂OH.

Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

- 5 Preferred water dispersible cationic ester surfactants are the choline esters having the formula:

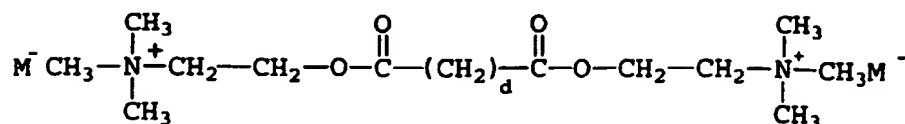
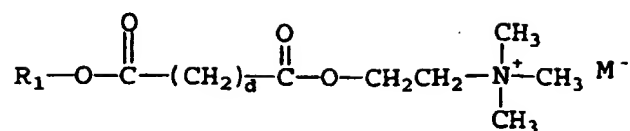


10 wherein R₁ is a C₁₁-C₁₉ linear or branched alkyl chain.

- Particularly preferred choline esters of this type include the stearoyl choline ester quaternary methylammonium halides (R¹=C₁₇ alkyl), palmitoyl choline ester quaternary methylammonium halides (R¹=C₁₅ alkyl), myristoyl choline ester quaternary methylammonium halides (R¹=C₁₃ alkyl), lauroyl choline ester methylammonium halides (R¹=C₁₁ alkyl), cocoyl choline ester quaternary methylammonium halides (R¹=C₁₁-C₁₃ alkyl), tallowyl choline ester quaternary methylammonium halides (R¹=C₁₅-C₁₇ alkyl), and any mixtures thereof.

- 20 The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, propylene glycol or preferably a fatty alcohol ethoxylate such as C₁₀-C₁₈ fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

- 30 Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.



In a preferred aspect the cationic ester surfactant is hydrolysable under the conditions of a laundry wash method.

5

Alkoxyated nonionic surfactant

Essentially any alkoxyated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

10

Preferred alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

15

Nonionic alkoxyated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

25

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably

30

C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R₂ is a C₅-C₃₁ hydrocarbyl, preferably straight-chain C₅-C₁₉ alkyl or alkenyl, more preferably straight-chain C₉-C₁₇ alkyl or alkenyl, most preferably straight-chain C₁₁-C₁₇ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic fatty acid amide surfactant

10

Suitable fatty acid amide surfactants include those having the formula: R⁶CON(R⁷)₂ wherein R⁶ is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R⁷ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and -(C₂H₄O)_xH, where x is in the range of from 1 to 3.

15

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

20

Preferred alkylpolyglycosides have the formula

25



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

30

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

35

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀-18 acylamido alkyl dimethylamine oxide.

- 10 A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

- 15 Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

20 Suitable betaines are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R^1 is typically C₁-C₃ alkyl, and R^2 is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂-18 dimethyl-ammonio hexanoate and the C₁₀-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine
25 surfactants are also suitable for use herein.

Cationic surfactants

Additional cationic surfactants can also be used in the detergent compositions herein.

- 30 Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

B. Source of Alkali

In accordance with the present invention, the alkalinity system is present in the detergent composition such that it has the capacity to react with the source of acidity to produce a gas. Preferably this gas is carbon dioxide, and therefore the alkali is a carbonate, or a suitable derivative thereof.

5

The detergent composition of the present invention preferably contains from about 2% to about 75%, preferably from about 5% to about 60%, most preferably from about 10% to about 30% by weight of the alkali source. When the alkali source is present in an agglomerated detergent particle, the agglomerate preferably contains from about 10% to about 60% of the alkali source.

10

In a preferred embodiment, the alkalinity source is a carbonate. Examples of preferred carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate, bicarbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Alkali metal percarbonate salts are also suitable sources of carbonate species and are described in more detail in the section 'inorganic perhydrate salts' herein.

15

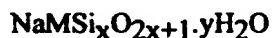
20 Other suitable sources will be known to those skilled in the art.

The alkalinity source may also comprise other components, such as a silicate. Suitable silicates include the water soluble sodium silicates with an $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred.

25 The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of 2.0 is the most preferred silicate. Alkali metal persilicates are also suitable sources of silicate herein.

Preferred crystalline layered silicates for use herein have the general formula

30



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is

35

preferably 2. The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

C. Source of Acidity

5

In accordance with the present invention, the source of acidity is present in the detergent composition such that the it is capable of reacting with the source of alkali to produce a gas.

10 The particle size of the source of acidity is calculated by sieving a sample of the source of acidity on a series of Tyler sieves. For example, a Tyler seive mesh 100 corresponds to an aperture size of 150 microns. The weight fractions thereby obtained are plotted against the aperture size of the sieves.

15 The source of acidity is preferably present at a level of about to about 15% by weight of the composition. Preferably up to about 10%, more preferably up to about 7% by weight. As previously mentioned it is advantageous to use as little of the source of acidity as possible, we have found that the present invention allows the use of levels as low as about 0.25% to about 5%. In a preferred embodiment of the present invention the source
20 of acidity is present in the range of about 1% to about 3%, most preferably about 3% by weight of the composition.

In accordance with the present invention, 80% or more of the acid source has a particle size in the range of from about 150 microns to about 710 microns, with at least about
25 37% by weight of the acid source having a particle size of about 350 microns or less. In a preferred embodiment 100% of the acid source has a particle size of about 710 microns or less, but this is not essential provided the aforementioned criteria are fulfilled. In another preferred embodiment of the present invention, greater than about 38%, more preferably 38.7%, of the particulate acid source has a particle size of about 350 microns
30 or less.

The source of acidity may be any suitable organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. The source of acidity may be a mono-, bi- or tri-protonic acid. Preferred derivatives include a salt or ester of the acid. The source of
35 acidity is preferably non-hygroscopic, in order to improve storage stability. Organic acids and their derivatives are preferred. The acid is preferably water-soluble. Suitable acids

include citric, glutaric, succinic or adipic acid, monosodium phosphate, sodium hydrogen sulfate, boric acid, or a salt or an ester thereof. Citric acid is especially preferred.

Additional detergent components

5

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

10

The compositions of the invention preferably contain one or more additional detergent components selected from additional surfactants, bleaches, builders, organic polymeric compounds, enzymes, suds suppressers, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

15

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

20

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

25

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

30

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and

35

fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates.

Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates
5 described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in
10 British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are
15 hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also
20 contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders
25 herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6
30 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

The detergent compositions of the present invention may contain a partially soluble or
35 insoluble builder compound, typically present at a level of from 1% to 80% by weight,

preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

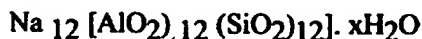
5

Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

10

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

15



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

20

Organic peroxyacid bleaching system

A preferred feature of detergent compositions of the invention is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

25

30

Inorganic perhydrate bleaches

35

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

5

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred

10 executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

15 Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to

20 $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

25 Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as

30

O

X - C - L

where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is

35

O

X - C - OOH

Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

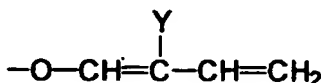
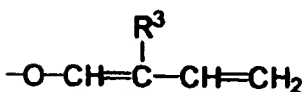
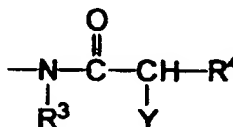
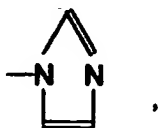
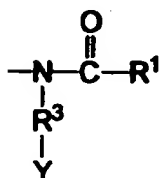
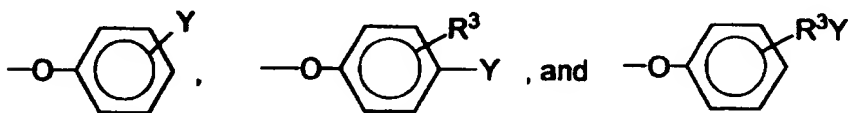
Leaving groups

15

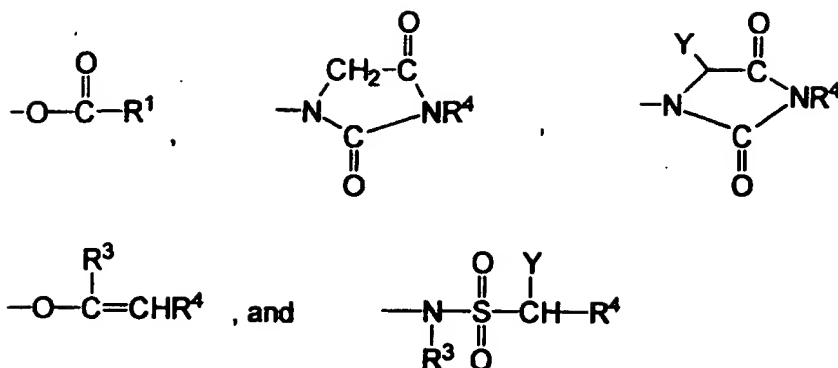
The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

20

Preferred L groups are selected from the group consisting of:



25



- and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.
- 10 The preferred solubilizing groups are $\text{-SO}_3^-\text{M}^+$, $\text{-CO}_2^-\text{M}^+$, $\text{-SO}_4^-\text{M}^+$, $\text{-N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}=\text{N}(\text{R}^3)_3$ and most preferably $\text{-SO}_3^-\text{M}^+$ and $\text{-CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with
- 15 sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl percarboxylic acid bleach precursors

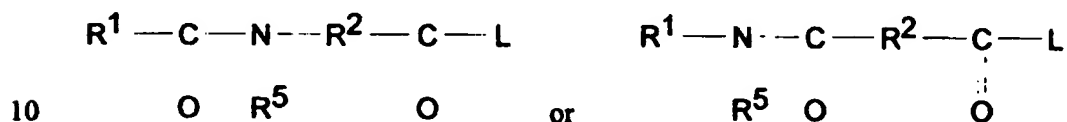
- 20 Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-, N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

5 Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

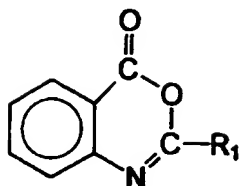
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

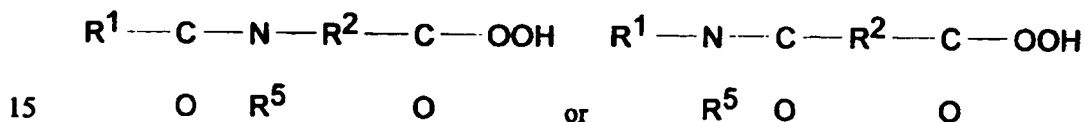


wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

5 Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach catalyst

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary

metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(\text{OCH}_3)_3(\text{PF}_6)$. Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4)^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

5 The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

10 Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

15 Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy diphosphonates and nitrilo trimethylene phosphonates.

20 Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

25 Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

30 Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

35

- EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS),
5 ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

- 10 Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

- Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases,
15 lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

- Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S
20 (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

- 25 Preferred amylases include, for example, α -amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo
30 Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

- Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to
35 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomonas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

5 Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

10 Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

15

Suds suppressing system

20 The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

25 Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

30

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl

35

group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake

copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

- 5 (c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

10 A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point
15 of from 45°C to 80°C.

Clay softening system

20 The detergent compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and
25 Gamble Company describe suitable organic polymeric clay flocculating agents.

Polymeric dye transfer inhibiting agents

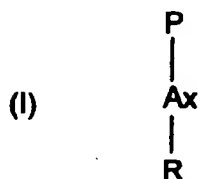
30 The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

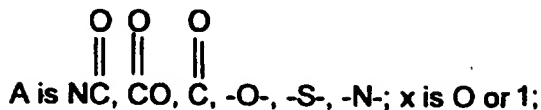
35

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

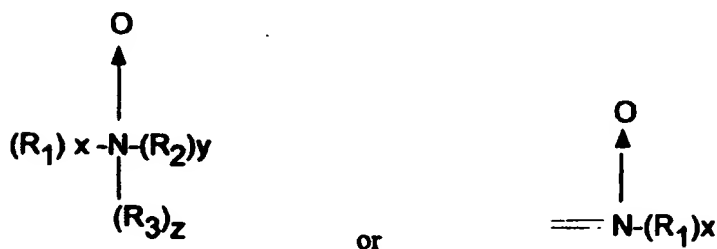


wherein P is a polymerisable unit, and



R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic,

alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides where to the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

35

d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000.

5

e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

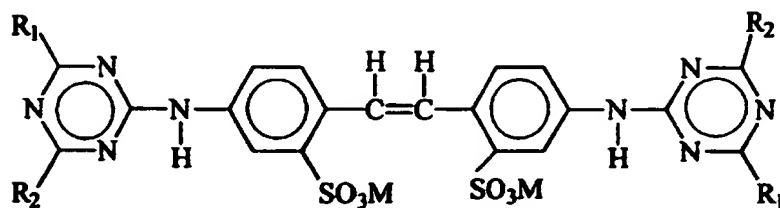
10

Optical brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

15

Hydrophilic optical brighteners useful herein include those having the structural formula:



20

wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morpholino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

30

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

pH of the compositions

The present compositions preferably have a pH measured as a 1% solution in distilled water of at least 10.0, preferably from 10.0 to 12.5, most preferably from 10.5 to 12.0.

Form of the compositions

The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing

machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

- 5 The mean particle size of the base composition of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

- 10 The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

- 15 The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an
- 20 axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

- 25 To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the
- 30 value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

- The composition is preferably soluble in cold or cool water, i.e. the composition readily dissolves/disperses in water at a temperature between about 0°C and 32.2°C, preferably
- 35 between about 1.6°C and 10°C.

Surfactant agglomerate particles

The surfactant system herein is preferably present in granular compositions in the form of surfactant agglomerate particles, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsennerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

- 15 A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used.
- 20 An operating temperature of the paste of 50°C to 80°C is typical.

- In an especially preferred embodiment of the present invention, the detergent composition has a density of greater than about 600 g/l and is in the form of powder or a granulate containing more than about 5% by weight of the alkali, preferably (bi-)carbonate or percarbonate. The carbonate material is either dry-added or delivered via agglomerates. The addition of the acid, preferably citric acid, (up to 10%) may be introduced into the product as a dry-add, or *via* a separate particle.
- 25

Laundry washing method

- 30 Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres,
- 35

as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

- In a preferred use aspect a dispensing device is employed in the washing method. The
- 5 dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.
- 10 Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during
- 15 the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

- To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may
- 20 be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

- 25 Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376,
- 30 EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly know as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one
5 washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked
10 wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent
15 Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water
20 impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in
25 any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European Application No. 94921505.7.

Example 1 - Comparative Performance Testing

30 The following experiments illustrate the benefits of using a formulation of the present invention, in which the source of acidity has the specified particle size distribution. More particularly we found that the formulation of the present invention showed a significant improvement at least in terms of the dispensing profile under stressed conditions (i.e. low
35 water pressure and temperature) compared to the same formulation without the source of acidity having the particle size distribution of the present invention.

Test Protocol

- 5 A Hotpoint automatic washing machine was employed, and a 2 minute 20°C cycle selected. 150 g of detergent dispensed via the dispenser drawer was used. The water flow rate into the machine was set at 2.0 l/minute.

The results are shown below in Table 1.

10 Table 1

Detergent	Detergent Density (approx.)(g/l)	Citric Acid Level (weight %)	% Detergent Residue in Dispenser Drawer (STD ¹)
Formulation I	730	-	40% (8%)
"	850	-	57% (6%)
"	850	0.8%	50% (4%)
"	850	1.5%	39% (3%)
"	850	2.0%	29% (1%)
Formulation II	850	-	50% (4%)
"	850	0.8%	41% (14%)
"	850	1.5%	39% (6%)
"	850	2.0%	27% (4%)

¹ Standard Deviation

- 15 The data shown in Table 1 was generated using a citric acid material with the particle size distribution shown in Table 2.

Table 2

Particle Size of Citric Acid ¹	Particle Size Distribution
> 710 microns	6.0%
425 - 710 microns	41.7%
355 - 425 microns	14.6%

250 - 355 microns ²	25.3%
150 - 250 microns	11.1%
< 150 microns	1.3%

¹Citric acid, monohydrate, fine granular, supplier Citrique Belge Ltd.

²The fraction with a particle size of greater than 355 microns was found to be 62.2% (STD 0.4%, 2 replicates). The estimated fraction with a particle size greater than 350
5 microns is 61.3%.

Abbreviations used in following Examples

10 In the detergent compositions, the abbreviated component identifications have the following meanings:

	LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
	TAS	:	Sodium tallow alkyl sulfate
	C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
15	CxyEzS	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
	C45E7	:	A C ₁₄₋₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
20	C25E3 average	:	A C ₁₂₋₁₅ branched primary alcohol condensed with an of 3 moles of ethylene oxide
	C25E5 average	:	A C ₁₂₋₁₅ branched primary alcohol condensed with an of 5 moles of ethylene oxide
	CEQ	:	R ₁ COOCH ₂ CH ₂ .N ⁺ (CH ₃) ₃ with R ₁ = C ₁₁ -C ₁₃
	QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
25	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
	TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
	TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
	STPP	:	Anhydrous sodium tripolyphosphate
30	Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ Si ₂ O ₂) ₁₂ . 27H ₂ O having a primary particle size
			in the range from 0.1 to 10 micrometers
	NaSKS-6	:	Crystalline layered silicate of formula

		δ -Na ₂ Si ₂ O ₅
	Citric acid	: Anhydrous citric acid
	Carbonate	: Anhydrous sodium carbonate with a particle size between 200 μ m and 900 μ m
5	Bicarbonate	: Anhydrous sodium bicarbonate with a particle size distribution between 400 μ m and 1200 μ m
	Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
	Sodium sulfate	: Anhydrous sodium sulfate
	Citrate	: Tri-sodium citrate dihydrate of activity 86.4% with a size distribution between 425 μ m and 850 μ m
10	particle	
	MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
	CMC	: Sodium carboxymethyl cellulose
	Protease	: Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
15	Alcalase	: Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
	Cellulase	: Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
20	Amylase	: Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
	Lipase	: Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
25	Endolase	: Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
	PB4	: Sodium perborate tetrahydrate of nominal formula NaBO ₂ .3H ₂ O.H ₂ O ₂
30	PB1	: Anhydrous sodium perborate monohydrate bleach of nominal formula NaBO ₂ .H ₂ O ₂
	Percarbonate	: Sodium Percarbonate of nominal formula 2Na ₂ CO ₃ .3H ₂ O ₂
35	NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.

- TAED : Tetraacetylenethylenediamine
- DTPMP : Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
- 5 Photoactivated : Sulfonated Zinc Phthlocyanine encapsulated in bleach dextrin soluble polymer
- Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl
- Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
- 10 HEDP : 1,1-hydroxyethane diphosphonic acid
- PVNO : Polyvinylpyridine N-oxide
- PVPVI : Copolymer of polyvinylpyrrolidone and vinylimidazole
- SRP 1 : Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
- 15 SRP 2 : Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
- Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
- 20 Alkalinity : % weight equivalent of NaOH, as obtained using the alkalinity release test method described herein.

25 In the following Examples all levels are quoted as % by weight of the composition:

Example 2

The following granular laundry detergent compositions A and B of bulk density 750 g/litre were prepared in accord with the invention:

30

	A	B
LAS	5.61	4.76
TAS	1.86	1.57

C45AS	2.24	3.89
C25AE3S	0.76	1.18
C45E7	-	5.0
C25E3	5.5	-
CEQ	2.0	2.0
STPP	-	-
Zeolite A	19.5	19.5
NaSKS-6/citric acid (79:21)	10.6	10.6
Carbonate	21.4	21.4
Bicarbonate	2.0	2.0
Silicate	-	-
Sodium sulfate	-	14.3
PB4	12.7	-
TAED	3.1	-
DETPMP	0.2	0.2
HEDP	0.3	0.3
Protease	0.85	0.85
Lipase	0.15	0.15

Cellulase	0.28	0.28
Amylase	0.1	0.1
MA/AA	1.6	1.6
CMC	0.4	0.4
Photoactivated bleach (ppm)	27 ppm	27 ppm
Brightener 1	0.19	0.19
Brightener 2	0.04	0.04
Perfume	0.3	0.3
Silicone antifoam	2.4	2.4
Citric acid	1.5	2.0
Minors/misc to 100%		

Example 3

- The following detergent formulations, according to the present invention were prepared,
 5 where C is a phosphorus-containing detergent composition, D is a zeolite-containing
 detergent composition and E is a compact detergent composition:

	C	D	E
Blown Powder			
STPP	14.0	-	14.0
Zeolite A	-	20.0	-
C45AS	9.0	6.0	8.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	9.0

TAS	2.0	-	-
CEQ	1.5	3.0	3.5
Silicate	7.0	8.0	8.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	26.0	23.0	25.0
PB4	18.0	18.0	10
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.25	0.30	0.15
Dry mixed sodium sulfate	3.0	3.0	5.0
Citric acid	2.5	2.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

	F	G
Blown Powder		
Zeolite A	15.0	-

Sodium sulfate	-	-
LAS	3.0	-
CEQ	2.0	1.3
DTPMP	0.4	-
CMC	0.4	-
MA/AA	4.0	-
Agglomerates		
C45AS	-	11.0
LAS	6.0	-
TAS	3.0	-
Silicate	4.0	-
Zeolite A	10.0	13.0
CMC	-	0.5
MA/AA	-	2.0
Carbonate	9.0	7.0
Spray On		
Perfume	0.3	0.5
C45E7	4.0	4.0
C25E3	2.0	2.0
Dry additives		
MA/AA	-	3.0
NaSKS-6	-	12.0
Citric acid	4.0	3.0
Citrate	10.0	8.0
Bicarbonate	7.0	5.0
Carbonate	8.0	7.0
PVPVI/PVNO	0.5	0.5
Alcalase	0.5	0.9
Lipase	0.4	0.4
Amylase	0.6	0.6
Cellulase	0.6	0.6
Silicone antifoam	5.0	5.0
Dry additives		
Sodium sulfate	0.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0

Density (g/litre)	700	700
-------------------	-----	-----

Example 5

The following detergent formulations, according to the present invention were prepared:

5

	H	I	J	K
LAS	12.0	12.0	12.0	10.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
CEQ	2.0	1.5	1.0	1.0
STPP	30.0	18.0	15.0	-
Silicate	9.0	7.0	10.0	-
Carbonate	15.0	10.5	15.0	25.0
Bicarbonate	-	10.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Citric acid	3.5	5.0	3.0	2.0
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 6

The following detergent formulations, according to the present invention were prepared:

5

	L	M	N
Blown Powder			
Zeolite A	10.0	15.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	10.0	8.0	10.0
C45AS	4.0	5.0	7.0
CEQ	2.0	2.0	2.0
Silicate	-	1.0	7.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	28.0	26.0	20.0
DTPMP	-	0.4	0.4
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	4.5
PBI	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
Citric acid	2.5	2.5	2.0
Balance (Moisture and Miscellaneous)	100	100	100

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	O	P
Blown Powder		
Zeolite A	15.0	15.0
Sodim sulfate	0.0	0.0
LAS	3.0	3.0
QAS	-	1.5
CEQ	2.0	2.0
DTPMP	0.4	0.4
CMC	0.4	0.4
MA/AA	4.0	2.0
Agglomerates		
LAS	4.0	4.0
TAS	2.0	1.0
Silicate	3.0	4.0
Zeolite A	8.0	8.0
Carbonate	8.0	6.0
Spray On		
Perfume	0.3	0.3
C45E7	2.0	2.0
C25E3	2.0	-
Dry additives		
Citric acid	2.0	3.0
Citrate	5.0	2.0
Bicarbonate	-	-
Carbonate	8.0	10.0
TAED	6.0	5.0
PB1	14.0	10.0
Polyethylene oxide of MW 5,000,000	-	0.2
Bentonite clay	-	10.0
Protease	1.0	1.0

Lipase	0.4	0.4
Amylase	0.6	0.6
Cellulase	0.6	0.6
Silicone antifoam	5.0	5.0
Dry additives		
Sodium sulfate	0.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0
Density (g/litre)	850	850

Example 8

- 5 The following high density detergent formulations, according to the present invention were prepared:

	Q	R
Agglomerate		
C45AS	11.0	14.0
CEQ	3.0	3.5
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
Citric acid	1.5	2.0
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0

TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

WHAT IS CLAIMED IS:

1. A detergent composition comprising a detergent surfactant, a particulate acid source and an alkaline source wherein said acid source and alkaline source are capable of reacting together to produce a gas, and wherein about 80% or more of the acid source has a particle size in the range of from about 150 microns to about 710 microns, with at least about 37% by weight of the acid source having a particle size of about 350 microns or less.
2. A detergent composition according to claim 1 wherein 100% of the acid source has a particle size of about 710 microns or less.
3. A detergent composition according to claim 1 or claim 2 wherein about 38.7% or more of the acid source has a particle size of about 350 microns or less.
4. A detergent composition according to any preceding claim wherein the alkaline source comprises a alkaline salt selected from an alkali metal or alkaline earth metal carbonate, bicarbonate, sesqui-carbonate, or alkali metal percarbonate salt..
5. A detergent composition according to any preceding claim wherein the acid source comprises an organic, mineral or inorganic acid.
6. A detergent composition according to claim 5 wherein the acid source is citric acid, glutaric acid, succinic acid, adipic acid, monosodium phosphate, sodium hydrogen sulfate or boric acid.
7. A detergent composition according to any preceding claim in the form of a granular detergent composition.
8. A detergent composition according to claim 4 wherein the acid source is added as a separate granular component.
9. A detergent composition according to any preceding claim wherein the alkaline source is present in an amount of from about 2% to about 75% by weight of the composition.

10. A detergent composition according to any preceding claim wherein the acid source is present in an amount of up to about 15% by weight of the composition.
11. A detergent composition according to any preceding claim wherein the composition further comprises a detergent builder.
12. A method of manufacturing the detergent composition of any preceding claim comprising mixing the detergent surfactant, particulate acid source and alkaline source.
- 10 13. A method of washing laundry in a domestic washing machine comprising, introducing into a dispensing device which is placed in the drum of the washing machine, or introducing into the dispensing drawer of a washing machine, an effective amount of a detergent composition of any one of claims 1 to 11.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/12894

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C11D 3/18, 3/10 US CL : 510/ 348, 349, 361, 406, 434, 477, 478, 509 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 510/ 348, 349, 361, 406, 434, 477, 478, 509 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS search terms: citric acid, carbonate#, deterg?, clean?, particle size, micron#		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0,534,525 A (UNILEVER PLC) 31 March 1993 (31-03-93), column 2, lines 55-59, column 3, lines 40-55, column 5, lines 30-40.	1-3
Y		1-3
X	US 5,540,855 A (BAILLELY ET AL) 30 July 1996 (30-07-96), column 2, lines 50-55, column 3, lines 10-15, column 12, lines 31-40, and example 1.	1-3
Y	US 5,268,283 A (MOTHES ET AL) 07 December 1993 (07-12-93), column 6, lines 5-10, column 8, lines 12-18, and lines 53-58.	1-3
Y	WO 92/18596 A (PANCHERI ET AL) 29 October 1992 (29-10-92), column 2, lines 23-31.	1-3
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family	
Date of the actual completion of the international search 15 OCTOBER 1997		Date of mailing of the international search report 17 NOV 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer KERY FRIES <i>Depe Walker</i> Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/12894

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-13
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.